ON THE NATURE AND ORIGIN OF PETROLEUM.

BY S. F. PECKHAM.

(Read February 5, 1897.)

Concerning the nature and origin of petroleum, I think we may say, after forty years of study and discussion, that we have not yet learned its alphabet with certainty. As petroleum is one of the forms of bitumen, in the line from natural gas to asphaltum, I do not think it has an origin independently of the other forms, and I shall therefore discuss the origin of bitumens together, as including petroleum.

Since I indulged my "Retrospect,"[1] two years ago last summer, two works have appeared which notably discuss the origin of bitumens, and I have in the course of my investigation of asphaltums and California petroleum, during the same period, noted a number of facts that bear upon the solution of this problem. In closing the "Retrospect" that I wrote while in southern California, and which was in part a reply to criticisms made by our friend, Prof. Orton, I remarked that I did not consider it necessary to represent in terms of Fahrenheit's thermometer the temperature at which any given specimen of petroleum was produced nor to produce the coke that resulted from the distillation. On reading over the paper since it appeared in print, I have feared that perhaps it had impressed some readers as dogmatic or as begging the question. It is sometimes difficult to express deep convictions with enthusiasm and not at the same time appear dogmatic. The Devonian shales, where they outcrop at Erie, Pa., have not apparently been subjected to alteration; yet, a number of wells drilled into them, have yielded an oil somewhat dense and of a bright green color. I believe that that oil was a product of distillation at a low temperature and under comparatively little pressure, the heat required being generated spontaneously within the shales. In Ventura county, southern California, metamorphism, that has resulted from some sort of action that has generated heat, has left masses of originally highly bituminous shale not only void of volatile matter but void of carbon as well. The expulsion of carbon is complete. The temperature must have been adequate, be the source of heat whatever

[1] *Am. Jour. Science* (3), xlviii, 389; Nov., 1894.

it may, yet there is no coke and no evidence that the temperature approached that of a brick kiln, nor such a temperature as in the ordinary processes of technology is found necessary to produce similar changes within periods of time upon which such processes are contingent. It was in the midst of such phenomena as I have just described and in the light of these facts that I then asserted that we cannot "reason from the processes of technology, bounded as they are by time and space, to the infinity of nature which it is impossible to imitate;" meaning that such reasoning cannot be applied to details.

A book was published in 1895, of which the eminent Swiss geologist, M. August Jaccard, was the author. The fact that it was a posthumous work leads one to pass lightly over mere blemishes of manner and style, and to note only those errors of judgment which led the author to erroneous conclusions. The book manifests a wide range of reading within the limits of publications in the French language, which has made it necessary that the author should confine himself to translations of the many memoirs that have appeared by English and American authors, and while the notices of such authors are frequently inadequate, few, if any, are omitted. M. Jaccard passes in review all of the different theories that have been proposed as a possible explanation of the phenomena observed in relation to the occurrence of bitumens in the Upper Valley of the Rhone, and discards all of those that regard bitumen as resulting from any cause or causes other than the alteration of animal remains by a special process of bituminization that has converted the organic matter directly into bitumen. He says, "distillation is an hypothesis absolutely destitute of proof" (p. 110), and, referring to the views of MM. Daubráe, Lartet and Coquand, he says further that "Their error consists in the fact of having confounded the formation of bitumen with the phenomena of its appearance (*reapparition*) at the surface which is posterior to it."

M. Jaccard then proceeds to set forth a system of nomenclature of his own and says, "It is in vain to wish to attempt a rational and systematic classification of natural hydrocarbons, solid and liquid and gaseous. It is in vain to set forth the multiplicity of names that have been applied to them by different authors. The expressions naphtha, petroleum, maltha, glutinous, viscous or solid bitumen, asphalt or pisasphalt, etc., are employed concurrently and without determined reasons. Their state, whether solid, liquid or gaseous, often depends upon the temperature at which they are at the moment when they are observed. . . . . Petroleum becomes solid when it has lost its light oils by exposure. They designate as asphalte a calcareous rock impregnated with bitumen, whilst if it be mixed with sand or gravel they apply the term petroleum" (p. 113).

"In presence of this uncertainty, it has appeared to me preferable to proceed to the study of the deposits by groups, and to adopt thus a purely methodical system.

"To this end I have established the four following groups:

"1. The asphaltic and bituminous deposits.

"2. The bituminous schists.

"3. The petroliferous and bituminous deposits.

"4. The natural combustible gas."

He then proceeds to discuss the subject along these inadequate and purely artificial lines, which time will not permit me to analyze in detail. It is sufficient for my purpose to say, that he concludes that bitumens have been produced in every case by a special decomposition of animal matter at the points where they are now found.

He thinks that because the bituminous limestones of Seyssel and Val de Travers are intercalated between beds of barren rock that the bitumen must have been formed *in situ*. That is by no means a necessary conclusion. The bitumen in a state of vapor, and probably accompanied by steam, expanded into the porous beds laterally, while passing through fissures in the compact and barren beds. When the Seyssel rock has been exhausted of its bitumen by chloroform and is examined under a microscope, it is found to be an amorphous mass of coarse-grained chalk with the finest particles one ten thousandth to one twenty thousandth of an inch in thickness—so fine that they pass through fine filter paper.

Any one familiar with the sea-shore has found shells of the common clam (*cardium*) filled with sand and saturated with the products of the decomposition of the soft parts of the bivalve dissolved in water. It is not an infrequent occurrence in regions where bitumen is abundant upon sea-coasts to find the shells of such bivalves filled with sand saturated with bitumen. The carbon contained in the solid or semi-solid bitumen required to saturate the dry sand that fills such shells is many times that found in the dried soft parts of the animal that occupied the shell. Such shells are common on and near the coasts of southern California. M. Jaccard calls attention to such shells as occurring in various places, but especially in the Val de Travers and its neighborhood, and seems to think they offer convincing proof that the bitumen originated where it is now found. Such an argument would never occur to one familiar with the sea-shore. The shells are first filled with sand and then saturated with bitumen, which enters them either as a liquid or hot vapor. I have seen multitudes of shells filled with bitumen and mixed with sand, fragments of shells, dirt, and crystallized carbonate of lime, none of which are a part of the animal that occupied the shell.

The second work to which I refer is the late monumental publication by Boverton Redwood, on Petroleum. After the most complete and wholly fair as well as the latest *resumé* of all the theories that have been advanced by the writers of both Europe and America, he sums up as follows:

"From the account given in this section, it will be seen that there has been an abundance of speculation as to the origin of bitumen and that, in regard to some of the theories, a considerable amount of experimental proof has been forthcoming. Probably, on the whole, the Höfer-Engler views at present have the largest number of adherents, and in respect, at any rate, to certain descriptions of petroleum, are the most worthy of acceptance. At the same time, a careful study of the subject leads to the conclusion that some petroleum is of vegetable origin, and it therefore follows that no theory is applicable in all cases."

Engler, like Warren, distilled fish oil and obtained petroleum-like products. He then distilled dried fish and other animal remains, and obtained altogether different products.

"Dr. Engler therefore considers that some change in the animal remains must have taken place in the earth, whereby all nitrogenous and other matters, save fats, were removed, the petroleum being formed from this fat alone, by the combined action of pressure and heat or by pressure only.

"In summing up the evidence as to origin, Höfer expresses the belief that petroleum is of animal origin, and has been formed without the action of excessive heat, and observes that it is found in all strata in which animal remains had been discovered."

Combining these two statements, we arrive at this conclusion as the Höfer-Engler theory, that bitumens are of animal origin, formed at low temperatures from fats alone by the combined action of pressure and heat.

Steam is left out of this formula and it is therefore inadequate. There is no evidence whatever that any portion of the crust of the earth has ever been subjected to the combined action of heat and pressure without the presence of steam or hot water, and in my judgment the steam has been a very potent factor in determining not only the formation but the transference of bitumens.

I have been many times told that the Turrellite of Texas consists of a mass of loose shells cemented together with bitumen. As it had that appearance, I never questioned the statement, until lately I had occasion to examine a specimen of this mineral. I pulverized some of it and proceeded to analyze it by solvents. I found that a portion of the mineral matter passed through fine filter paper. I then digested a piece of it in successive portions of chloroform, until the chloroform was no longer colored. There remained a white shell-rock, or coquina, quite firm and strong, very light in weight, with the cavities of some of the shells partly filled with crystallized rhomb-spar; together with fragments of shells and dust. Under the microscope some of the dust was only one twenty thousandth of an inch in thickness. The shells had been subjected to the action of hot water after all traces of the soft parts of the animals had disappeared and a part of the lime had been dissolved and redeposited in the cavities of the shells and between them, thus cementing them together; and this anterior to the entrance of the bitumen, which must have filled the shell-limestone as a vapor or in a fluid or semi-fluid condition. When separated from the shells the bitumen is very pure and uniform in its composition, containing many times the amount of carbon that existed in the soft parts of the animals that made the shells their home. The porous shell-rock simply afforded an adequate receptacle for the bitumen that was distilled or sublimed into it.

I have lately examined California petroleums more closely than I ever had before. I have distilled off the lightest portion from some Wheeler's Cañon green oil that I took from the Cañon in 1866. I also distilled about fifty per cent.—the lightest portion—from some Pico Cañon oil that I got from there two years ago. While in California in the fall of 1894, I distilled from several samples of black oil, taken from wells in the Sespè and Torrey Cañons and near Bardsdale, about twenty-three per cent. of the lightest portion. The distillation was conducted in a common tubulated glass retort with a thermometer introduced into the tubulure in such a manner as to indicate the temperature at which the condensing vapor passed over. This was the first time I had ever distilled these oils in such an apparatus, and some of the results observed were exceedingly interesting. The crude oils contained a little water, as all petroleums do, which came over with the light distillate, at or below 100° C. As the boiling point of the oil and the temperature of the condensing vapor arose, at 120°–140° C., water again appeared. The two portions of water distilled over at temperatures separated by at least 30° C. The last portion appeared, in part, as an emulsion that collected in white drops upon the neck of the retort, and, gathering, ran through the condenser to the receiver, where it fell through the column of oil and collected as water at the bottom of the receiver. On standing twelve hours, small spots and patches in the neck of the retort appeared of a purple color, and a deposit that resembled argol appeared as a precipitate in small quantity at the point of contact between the oil and water in the receiver. While an appreciable amount of this precipitate appeared in the distillate from the black oil, only a trace was present in the distillates from the oils from the Pico and Wheeler's Cañons. With sulphuric acid, followed by sodium hydrate, this precipitate gave a qualitative reaction for one of the esters of the pyridin bases; that is to say, dilute sulphuric acid dissolved a part of it, leaving a purple residue, and from the sulphuric acid solution sodium hydrate precipitated white flakes having the odor of pyridin. The distillates also gave the usual reaction for these esters in small quantities. Fractionated in a bulb apparatus with beads, the distillate from black oil has yielded "heaps" corresponding to the boiling points of the benzoles and naphthenes. This work is still incomplete.

The facts of greatest interest, however, in reference to these oils, that this latest work has demonstrated, relates to their sulphur content. An observation that I made many years ago has been often quoted, that in one instance I distilled a California oil that contained so much sulphur that the sulphur condensed in the neck of the retort. As I remember the experiment, the amount of oil distilled was about half a litre; and a button of pure sulphur condensed in the neck of the retort at least half a centimeter in diameter. This oil was from the Cañada Larga spring, which issues from strata containing a large amount of free sulphur. I have never seen another California oil from which this experiment could be repeated; and I have long since concluded that the sulphur was in this instance dissolved in the oil.

While in California a few years ago, I was engaged in distilling these petroleums in quantities ranging from a few gallons to thousands of barrels. I looked in vain for any evidence that they were sulphur petroleums. It was only after I had begun fractioning the light oils—a work for which I had not the proper appliances in California—that I began to suspect that there were sulphur compounds present, and at last discovered that, with the thermometer bulb immersed in the condensing vapor, even at a temperature as low as 100° C., the distillates were decomposed and hydrogen sulphide disengaged. This decomposition of the oil was accompanied by a deposition in the flask of carbon, or a compound so rich in carbon that it remained undissolved in either the distillate or residual oil, and also by condensation of the residual molecule, as indicated by a continual rise in the boiling point of the oil remaining in the flask.

These observations have led me to conclude that sulphur as well as nitrogen plays a part in the changes which are active in the natural conversion of petroleum, through maltha, into asphaltum. That the esters exist as acid salts of the basic oils is quite probable; that polymerization of the molecules occurs to some extent cannot be doubted; that decomposition of the sulphur compounds takes place very slowly and at comparatively low temperatures with condensation of the residual molecules is almost certain; and that removal of hydrogen in the oil through deoxidation of the sulphates in the water with which the bitumens are in constant contact, with substitution of sulphur, may all be accepted as the prime factors of the problem involved in these changes. The lines of investigation above indicated have led me to some very interesting work upon the sulphur content of other bitumens than petroleum, which work is as yet incomplete.

Closely related to these factors are some observations made during my last visit to California. It was noticed that when the oils conveyed through pipe lines were distilled in summer, the yield of naphtha was much less than was obtained from the same oils in winter, although the extremes of temperature were not great. Upon investigation I found that in October, 1894, the oil, flowing through the blackened pipes laid upon the surface, was discharged into the tanks at a temperature of 90° F. I also found that an oil fresh from a well, kept in an open vessel at a temperature of about 100° F. for four days, ceased to lose weight and decreased in volume twenty-five per cent. In another experiment, one litre of oil was exposed to the sun in a pan placed in a window seat for three days. The temperature was at no time above 90° F., and over half of the time was below 70° F. The loss was twenty per cent. by volume, and the specific gravity changed from 28.5° B to 20.2° B. These results show that at the surface, natural evaporation is also a potent factor in the conversion of petroleum into maltha and asphaltum.

I wish to note here several facts of a different order bearing upon these questions. In 1865–6 the carcasses of several whales were lying half buried in the sand of the Pacific coast, between Point Conception and Ventura, California. They furnished food for numerous vultures and buzzards, and while the odor was not agreeable, it was the odor of rancid fat rather than of putrid flesh. During the summer of 1894 a vast number, weighing many tons, of deep sea fish, in a dying condition, came ashore upon that same coast for at least two hundred miles. Many of these fish were of large size, and among other species was a basking shark, twenty-six feet in length. An examination by one of the officers of the State Fish Commission led to the discovery that the gills of these fish were more or less filled with bitumen, which constantly rises from the bed of the ocean off this coast. The destruction of animal life was enormous. The first gale with a high tide buried nearly all of the fish in the sand of the beach. Complete skeletons of whales have been repeatedly discovered in the petroleum-bearing strata of that region, some of them saturated with bitumen.

One hundred miles due north of this coast, on the other side of the Coast Ranges, I have examined some of the most extensive veins of asphaltum yet discovered. They have been traced across the country continuously for miles and have been mined to a depth of more than three hundred feet. In chemical composition the asphaltum bears a specific relation to the petroleums of Ventura county. They both contain the esters of the pyridin bases. These asphaltum veins lie on one side of and irregularly parallel with a stratum of sandstone, which, like all of the strata of that region, stands nearly vertical. Along this sandstone stratum bitumen exudes for a long distance. Against it, and on the other side of it, rests a bed of infusorial earth, at least 1000 feet in thickness, in some places saturated with bitumen, but for the most part clean and white. These formations extend across the country, parallel for miles with the general trend of the Coast Ranges. Enormous springs of maltha, issuing therefrom at intervals, have produced at several points flood-plains of asphaltum that fill the small valleys like a glacier, many feet in depth and square miles in extent. The maltha is invariably accompanied with water, and at several points there are evidences that at some period in the past history of those outflows the springs that are now cold have been gigantic hot springs of silicated water, similar to those that I believe produced the famous Pitch Lake of Trinidad.

I went to Trinidad prepared to find abundant evidence of the direct conversion of wood into bitumen, as described by Wall and Sawkins. I saw nothing of the kind; nor could I find any one else who had. A superstition among the natives ascribes to the black mangrove the power of secreting bitumen. This shrub grows with its roots in sea water and often covered with oysters. The movement of the tide, the most nearly eternal phenomenon in nature, bears the bitumen that rises from the bottom of the sea against the oyster shells, and their jagged edges gather the floating particles. The entire deposit of pitch, both within and without the lake, contains on an average ten per cent. of partially decayed vegetation, and also an amount, difficult to estimate, of branches, trunks and stumps of trees, some of the latter of enormous size, much larger than any now standing in the vicinity. I did not see the outcrop of the lignite bed to the south of the lake that dips at an angle that would send it under the lake, as described by Manross, but I was told by one who had seen it, that this lignite bed, twelve feet in thickness, contained branches, trunks and stumps of trees that were in exactly the same condition as those found in the pitch —that is, they were still wood—not having been changed into lignite, and therefore not capable of being distilled by hot silicated water into pitch.

The circumstances of my life have brought me into personal contact with deposits of bitumen over a very wide area, and under such conditions as have afforded me very unusual opportunities for a careful study of all the phenomena attending the appearance of bitumen at the surface of the earth; the result of which has been to confirm the opinion that I have heretofore expressed, that, in the majority of instances, bitumens, from natural gas to asphaltum, are, where we now find them, distillates. In making this declaration I do not wish to be understood as calling in question the correctness of either the observations or opinions of those who have reached different conclusions.

Perhaps fifty years from now our ghosts may sit here with our grandchildren and hear them dogmatize concerning the origin of bitumen. For myself, the longer I study the subject and the wider my experience becomes, the less I am prepared to assert that any formula is capable of universal application. I would therefore suggest, that, as we now find them, bitumens are in some instances still where they were originally produced by a process of decomposition of animal remains, that is at present being illustrated on a small scale in the shallow bays of the Red Sea. Further, that other deposits contain primary distillates from the vegetable and animal remains enclosed in geological formations that have been invaded by heat, steam and pressure in past periods of the earth's history; and finally, that in some instances, as we now know them, bitumens have been transferred and stored by a secondary invasion of bituminous deposits by heat, steam and pressure. The details of these various movements await for their expression a vast amount of chemical and geological research by those who are to come after us.

A SUGGESTION AS TO THE ORIGIN OF PENNSYLVANIA PETROLEUM.

BY DAVID T. DAY.

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The three general classes of theories as to the origin of petroleum are so well known as to call for no especial description. I refer to (1) the inorganic origin by the action of water on metallic carbides; (2) by the slow decomposition of vegetable remains with insufficient supply of air, with or without simultaneous production of coal; and (3) the distillation of the fatty portion of anima organisms under pressure, in accordance with the discoveries generally credited to Engler.

It is pleasant, however, to recall attention to the fact, which has frequently been lost sight of, that Warren and Storer first distilled petroleum from animal fats years before; that is by the distillation